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CONTINUOUS MANUFACTURING METHOD OF CLAD-TYPE HIGH-PURITY FUSED SILICA ROD

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Reference cited: U.S. Patent No. 3,117,838

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Claim

A continuous manufacturing method of a clad-type high-purity fused silica rod characterized by the following facts: this is a manufacturing method of clad-type high-purity fused silica rod using equipment having a configuration that enables relative driving between a rotating rod holder and a heat treatment unit using a gas flame; on the surface of the rod made of a transparent silicon compound glass, micron-sized powder of a silicon compound is deposited uniformly and finely by means of flame oxidation decomposition of the silicon compound or a mixture of the silicon compound and impurity with added hydrogen gas in an amount 25-35X that of the silicon compound vapor; then,

the micron-sized powder of the aforementioned deposited silicon compound is subjected to continuous heat treatment by the oxygen/hydrogen flame so that a transparent vitreous coating is fused.

Detailed explanation of the invention

This invention pertains to a continuous manufacturing method of a clad-type high-purity fused silica rod used as a material for optical transmission line.

The glass fiber optical transmission line for optical communication is usually made of a core and cladding. Suppose the refactive indices of the core and cladding of the optical transmission line are n_1 and n_2, respectively; there is the following relationship:

$$n_2 = n_1 (1 - \Delta)$$

where Δ is in the range of about 10^{-2} to 10^{-3}, and depends on the wavelength of the light for transmission. Consequently, it is necessary to have only a very small difference between n_1 and n_2. Also, in order to reduce the attenuation of the light, it is necessary to reduce the application and scattering by the material itself. When light is transmitted through the core, there is a loss in the light due to interference by the impurity in the core material and due to scattering caused by bubbles, foreign objects, and the material itself. Also, the bubbles, foreign objects, etc., at the interface between the core and the cladding are also a major cause of the loss by scattering.

When the optical fiber is manufactured from the clad-type

optical transmission line feed material, the material corresponding to the core is inserted into the pipe corresponding to the cladding, followed by processing into the fiber. In this case, the scattering loss caused by bubbles and foreign objects at the interface between the core and the cladding is the most serious disadvantage.

In order to improve the aforementioned method, several methods have been proposed in Japanese Kokai Patent Application Nos. Sho 49[1974]-9523, Sho 49[1974]-10055, Sho 49[1974]-10056, Sho 49[1974]-18909, etc. For example, in the method disclosed in Japanese Kokai Patent Application No. Sho 49[1974]-9523, by means of flame hydrolysis of the silicon compound, a soot-like deposit is attached to the core of a nonmetal refractory material (graphite or refractory ceramics); the soot-like deposit is then sintered, and the rod is inserted slowly into an rf inductive heating oven at 1400-1700°C in an inert atmosphere, at a speed appropriate for enabling escape of the adsorbed gas from the unsintered portion, forming a transparent vitreous cladding. However, as the rod with the soot-like deposit on it is inserted into the rf inductive oven very slowly, the sintering operation takes a long time, and the demand on control of the quality characteristics becomes complicated. This is unfavorable for production. Also, as graphite is used as the core material, if the atmosphere used is not highly inert, influence by impurities may take place easily in the rf inductive heating oven, and contamination may take place easily. This is a disadvantage. In addition, in the process of sintering of the soot-like deposit layer in the rf inductive heating oven, as heating is performed from the surface of the soot-like deposit, it is difficult to

completely remove the gas bubbles hidden inside the rod. This is also a disadvantage. For the optical transmission line material manufactured using this method, as the soot-like deposit layer is sintered to form a vitreous cladding, which is not bonded to the core material (graphite), when it is used as an optical transmission line, the inner surface of the cladding must be mechanically polished. This is a disadvantage.

The purpose of this invention is to solve the problems of the aforementioned conventional method by providing a continuous manufacturing method of clad-type high-purity fused silica rod as an optical transmission line material. That is, this invention provides a continuous manufacturing method of clad-type high-purity fused silica rod characterized by the following facts: this is a manufacturing method of clad-type high-purity fused silica rod using equipment having a configuration that enables relative driving between a rotating rod holder and a heat treatment unit using a gas flame; on the surface of the rod made of a transparent silicon compound glass, micron-sized powder of a silicon compound is deposited uniformly and finely by means of flame oxidation decomposition of the silicon compound or a mixture of the silicon compound and impurity with added hydrogen gas in an amount 25-35X that of the silicon compound vapor; then, the micron-sized powder of the aforementioned deposited silicon compound is subjected to continuous heat treatment by the oxygen/hydrogen flame so that a transparent vitreous coating is fused.

In the following, this invention will be explained in more detail with reference to an application form illustrated by the attached figure. As shown in this figure, a mixture of silicon

compound and impurity is fed through burner (2) onto the surface of a transparent silicon compound glass rod (1), and micron-sized powder (3) is deposited by means of flame oxidation decomposition. Said silicon compound glass rod (1) has one end held by a rotating rod holder (not shown in the figure) and is driven to rotate at a prescribed rotating speed. Then, immediately after deposition of the aforementioned micron-sized powder, deposited micron-sized powder (3) is subjected to flame heat treatment by oxygen/hydrogen flame burner (4), so that it is fused to form a transparent vitreous cladding (5).

More specifically, as the silicon compound, silicon hydride or silicon chloride is usually used. The preferable types include SiH_4, $SiHCl_3$, $SiCl_4$, and SiH_2Cl_2, etc. For SiH_4 and SiH_2Cl_2, they may be fed in vapor form through burner (2). On the other hand, for $SiCl_4$ and $SiHCl_3$, as it is in liquid form at room temperature, it is necessary to feed them by means of a carrier gas, such as H_2, Ar, O_2, etc., through burner (2). The impurities doped into the silicon compound include B_2H_6, BCl_3, BBr_3, etc. It is preferred to use B_2H_6 and BCl_3, as they can be used preferably as vapor at room temperature. As the aforementioned feed vapor is fed together with H_2 and O_2 to burner (2), a flame is formed, and micron-sized powder of about 1 μm is formed and deposited on the surface of core (1). In the aforementioned burner, by means of flame oxidation decomposition, a fine and uniform [layer] of the micron-sized powder with a size of about 1 μm can be formed at a high efficiency. It is preferred that the amount of the hydrogen gas fed with respect to the amount of the vapor of silicon compound fed to the burner be in the range of 25-35X. If

the amount of the hydrogen gas fed with respect to the amount of the silicon compound vapor fed is less than 25X, the micron-sized powder formed is not uniform, and foaming may take place easily. On the other hand, if the amount of hydrogen gas fed with respect to the amount of the silicon compound vapor is over 35X, the relative amount of the silicon compound vapor becomes smaller, and the amount of the micron-sized powder deposited becomes smaller. For micron-sized powder (3) deposited on the surface of core (1), the deposit pattern is made of symmetric cones on both sides from burner (2) at the center. Deposit layer (3) of micron-sized powder in the deposition starting portion (the righthand side in Figure 1) is remote from the outer flame of fusing burner (4), and is thus soft. As said soft deposit layer (3) enters the outer flame of burner (4) for fusion under driving by core (1), it is sintered and gradually becomes hard (the lefthand side of deposit layer (3) in Figure 1). In addition, as it enters the flame of burner (4) for fusion, the sintered portion enters a semimelted state, and it gradually becomes transparent and vitreous from the interface. At this time, the gas adsorbed inside the semimelted portion gradually escapes to the unsintered portion. Consequently, transparent vitreous cladding (5) becomes free of bubbles, and no bubbles are generated at the interface between core (1) and transparent vitreous clad (5). The aforementioned core may be made of the commercially available high-purpose transparent fused silica glass rod. It is preferred that there are no fine scratches on the surface. More preferably, the surface may be processed by polishing to optical grade. When there are scratches or embossed pattern on the core material, it is difficult for the bubbles to

escape completely when the cladding is sintered, and bubbles may remain on the scratches and embossed portion of the core. In addition to the high-purity fused silica glass rod, it is also possible to use a glass doped with elements for increasing the refractive index. In addition, if the core is too fine, deformation under influence of the burner may take place easily. Consequently, it is preferred that a rod with diameter of 2 mm or larger be used.

Application example

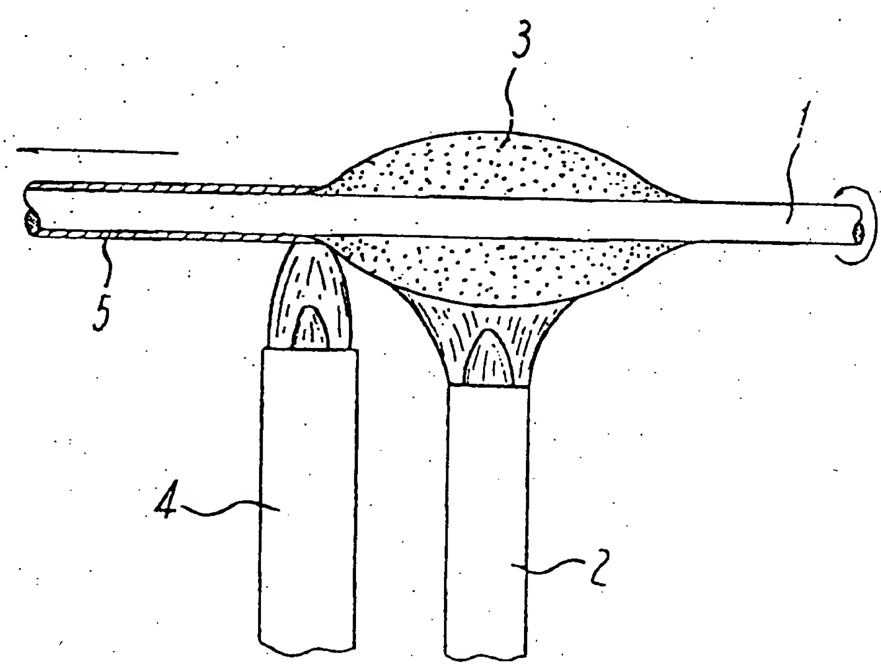
A 3-mm-diameter high-purity fused silica glass rod, which had been subjected to grinding to optical grade, was held as a core on a rotating rod holder. While the aforementioned core was rotated at a speed of 4 rpm and was driven to move at a speed of 2 mm/min, 0.05 L/min of SiH_4 gas, 0.015 L/min of BCl_3, 2.35 L/min of O_2 gas, 1.5 L/min of H_2 gas, and 1.2 L/min of Ar gas were fed for flame oxidation decomposition, and the micron-sized powder was deposited. Immediately after that, flame heat treatment was performed by an adjacent burner for fusion with 1.12 L/min of O_2 gas and 3.7 L/min of H_2 fed to it. In a single round of operation, a transparent vitreous clad with [thickness] of about 1.5 mm was formed. For the clad-type material prepared in this application example, the difference in the refractive index is 0.4%. When the optical fiber formed from it was measured, it was found that the loss was 3.5-4.6 db/km for a wavelength of 0.63-0.8 μm, respectively.

As explained above, in this invention, a transparent vitreous cladding can be formed in a single round of operation by means of the continuous heat treatment using a gas flame. Consequently, it is possible to form a high-quality optical transmission line material that is free of contamination, and with high uniformity at the interface between the core and the cladding. Also, the method of this invention can significantly increase productivity.

Brief explanation of figures

The attached figure is a partially cut longitudinal cross-sectional view illustrating an implementation form of this invention.

1. Core
2. Burner for flame oxidation decomposition
3. micron-sized powder deposited on the core
4. Burner for fusion
5. Fused transparent silicon compound glass cladding, with arrow indicating the direction of movement of the core.



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発明の数 1

(全 3 頁)

1

㊿クラッド型高純度石英棒の連続製造方法

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㊼特許請求の範囲

1　回転可能な棒保持装置とガス状火炎の熱処理装置とが相対的に駆動可能な如く構成された装置を使用してクラッド型高純度石英棒を製造する方法において、透明珪素化合物系ガラス棒状体の表面に、珪素化合物または珪素化合物と不純物との混合物を珪素化合物ガスに対して25～35倍の水素ガスを含む火炎酸化分解によつて均一かつ緻密な珪素化合物系の微粉末を沈積させ、引き続いて前記沈積された珪素化合物系の微粉末を酸水素火炎による連続熱処理によつて透明なガラス状被覆を融着させることを特徴とするクラッド型高純度石英棒の連続製造方法。

発明の詳細な説明

本発明は光伝送路用材料となるクラッド型高純度石英棒の連続製造方法に関するものである。

一般に光通信用のガラスフアイバー光伝送路は、芯部(コアー)および被覆部(クラッド)から構成されている。かかる光伝送路の芯部および被覆部の屈折率をそれぞれn_1, n_2とすれば、

$$n_2 = n_1(1-\Delta)$$

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という関係にありΔは伝播する光の波長によつて10^{-2}～10^{-3}程度となり、したがつてn_1とn_2は極めて僅かの差をもつことが必要であり、かつ伝播される光の減衰を小さくするためには材料自体の吸収および散乱損失を減らさなければならない。光はコアー部を伝播していくので主としてコアー材料の不純物による吸収、泡、異物および材料自体からくる散乱などの種々の損失が問題であるが、その他にもコアーとクラッドの界面の泡、異物等が散乱損失の大きな原因となつている。

またクラッド型光伝送路素材からフアイバーを製造する場合、クラッドとなる管の中にコアーとなる芯材を挿入して、フアイバーに加工し一体とする方法をとつていたが、この場合コアーとクラッドの界面の泡、異物による散乱損失が大きく最大の欠点となつていた。

かかる前記方法の改良法としては、既に特開昭49－9523号公報、特開昭49－10055号公報、特開昭49－10056号公報、特開昭49－18909号公報所載の技術等が提案されている。例えば特開昭49－9523号公報には、珪素化合物の火炎加水分解により非金属性耐火物(黒鉛または耐火性セラミック)の芯にすす状析出物を付着させ、すす状析出物が焼結し、しかも吸蔵ガスが未焼結部から逃げるに充分な速度で徐徐に不活性雰囲気の1400～1700℃の高周波誘導加熱炉の中へ挿入して透明ガラス状の被覆層を得るという方法であるが、すす状析出物を付着させてしかる後に高周波誘導加熱炉に極めてゆつくり挿入して焼結するために工程および時間が長くかかり、品質特性の制御要素は増加し生産的ではない。また芯に黒鉛を用いるために特に不活性雰囲気を用いなければならず、高周波誘導加熱炉内での不純物の影響を受け易く汚染の機会が多いという問題点があり、さらには高周波誘導加熱炉内での沈積されたすす状析出物層の焼結過程は、すす状析出物層の表面から加熱していくために内

部の気泡が完全に抜けにくいという欠点もある。かかる方法で製造された光伝送路用材料は、すす状析出物層を焼結してガラス化した被覆層と芯材（黒鉛）とは密着してはいないが、光伝送路として使用する場合には被覆層の内面を機械的研磨仕上げを必要とする欠点もある。

本発明は上記欠点および問題点を解消した光伝送路用材料であるクラッド型高純度石英棒の連続製造方法を提供するものである。即ち、回転可能な棒保持装置とガス状火炎の熱処理装置とが相対的に駆動可能な如く構成された装置を使用してクラッド型高純度石英棒を製造する方法において、透明珪素化合物系ガラス棒状体の表面に珪素化合物または珪素化合物と不純物との混合物を、珪素化合物ガスに対して25〜35倍の水素ガスを含む火炎酸化分解によつて均一かつ緻密な珪素化合物系の微粉末を沈積させ、引き続いて前記沈積された珪素化合物系の微粉末を酸水素火炎による連続熱処理によつて透明なガラス状被覆層を融着させることを特徴とするクラッド型高純度石英棒の連続製造方法である。

次に本発明の一実施態様を添附図面に基づいて説明する。図示の如く回転駆動する透明珪素化合物系ガラス棒状体1の表面に珪素化合物または珪素化合物と不純物との混合物をバーナー2に所定の量を供給し、火炎酸化分解を行つて微粉末3を沈積させる。前記珪素化合物系ガラス棒状体1はその一端を回転駆動可能な保持具によつて保持され（図示していない）、所定の回転数および駆動速度で回転駆動されている。引き続いて、前記微粉末の沈積後直ちに隣接して設置された酸水素炎バーナー4によつて沈積された微粉末3を火炎熱処理することによつて融着し、透明なガラス状被覆層5を形成するのである。

さらに詳述すれば、珪素化合物には通常珪素の水素化物または塩化物が使用されるがSiH_4，$SiHCl_3$，$SiCl_4$，SiH_2Cl_2等を使用するのが望ましい。SiH_4，SiH_2Cl_2の場合はガス状バーナー2に供給すれば良いが$SiCl_4$，$SiHCl_3$は常温では液体なのでH_2，Ar，O_2等をキャリヤーガスとしてバーナー2に供給することが必要である。珪素化合物に添加する不純物には通常B_2H_6，BCl_3，BBr_3等が使用されるが、B_2H_6，BCl_3は常温でガス状であるから使用する場合は有利である。前記の原料ガスとH_2およびO_2をバーナー2に供給して火炎を形成して生成した1μ程度の微粉末を芯材1の表面に沈積させる。前記バーナーにおける火炎酸化分解で、緻密で均一な1μ程度の微粉末を効率良く得るためには、バーナーに供給する珪素化合物ガス量に対して水素ガス供給量を25〜35倍の量にするのが好ましい。珪素化合物ガス供給量に対して、水素ガス供給量が25倍未満では、生成される微粉末が均一でなくなるので泡が発生しやすくなる。また珪素化合物ガス供給量に対して水素ガス供給量が35倍を超えると、珪素化合物ガスが相対的に少なくなるから微粉末の沈積量が少なくなる。芯材1の表面に沈積された微粉末3はバーナー2の中心から見て左右円錐状に沈積され、沈積開始部分の微粉末沈積層3（第1図の右側）は隣接せる融着用バーナー4の外炎からはずれるから柔らかい。前記柔らかい沈積層3は芯材1の駆動にともなつて融着用バーナー4の外炎に入るにしたがい徐々に焼結されかたくなつていく（第1図沈積層3の左側）。さらに融着用バーナー4の火炎中に入つてくると焼結部は半溶融状態になり、界面から徐々に透明ガラス状に変化するのである。この時半溶融部の内部に吸蔵されているガスは外部の未焼結部へ徐々に逃げて行くために透明ガラス状被覆層5には泡がなく、また芯材1と透明ガラス状被覆層5との界面にも泡が生じない。前記芯材には市販の高純度透明石英ガラス棒でも良いが、その表面に細かいきずの無いものが有利であり、望ましくは表面を光学研磨したものが良い。これは芯材にキズや凹凸があると被覆層焼結の際に泡が完全に逃げにくく芯材のキズや凹凸面に泡が残り易いからである。前記芯材には高純度透明石英ガラスのほかに屈折率を高めるための元素が添加されたものも使用可能である。さらには芯材があまり細いとバーナー火炎の影響によつて変形してしまうことがあるので直径2mm以上のものを使用するのが有利である。

実施例

回転駆動可能な棒保持装置に光学研磨をほどこした直径3mmの高純度石英ガラス棒を芯材として保持した。前記芯材を毎分4回転、駆動速度毎分2mmの速さで移動させながら先ず芯材の表面にSiH_4ガス0.05ℓ/min，BCl_3ガス0.015

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／min、O_2 ガスを2.35ℓ／min、H_2 ガス1.5ℓ／min、Arガスを1.2ℓ／minの割合で供給し火炎酸化分解によつて微粉末を沈積し、直ちに隣接せる融着用バーナーにO_2 ガスを1.12ℓ／min、H_2 ガス3.7ℓ／minの割合で供給して火炎熱処理をしたところ、1回の操作で約1.5mmの透明ガラス状被覆層を得た。上記実施例で得たクラッド型材料は屈折率差が0.4%であり、またフアイバーにした場合の損失を測定したところ0.63μm～0.8μmでそれぞれ3.5db／km～4.6db／kmであつた。

以上詳述せる如く本発明によればガス状火炎の連続熱処理の1回の操作で透明ガラス状被覆層を形成するので汚染されず、しかも容易に芯材と被

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覆層との界面を均一にすることが出来高品質の光伝送路用材料が得られるようになつた。また本発明法によつて生産性の向上は格段に進歩した。

図面の簡単な説明

添附図面は本発明の一実施態様を示す一部縦断面図で、1……芯材、2……火炎酸化分解用バーナー、3……芯材上に沈積された微粉末、4……融着用バーナー、5……融着された透明珪素化合物系ガラス被覆層、矢印は芯材の移動方向および回転方向を示す。

56引用文献
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